Food Chemistry 175 (2015) 439–444

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Furan formation from fatty acids as a result of storage, gamma irradiation, UV-C and heat treatments ☆

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ARTICLE INFO

Article history:
Received 11 April 2014
Received in revised form 9 October 2014
Accepted 2 December 2014
Available online 9 December 2014

Keywords:
Furan
Fatty acid
Thermal
UV
Ionizing radiation
Linoleic acid
Linolenic acid

ABSTRACT

The effects of gamma and UV-C irradiation in comparison with thermal processing and storage at 25 °C on formation of furan from different fatty acids were investigated. Results showed that furan was generated from polyunsaturated fatty acids such as linoleic and linolenic acid during thermal (120 °C, 25 min) and UV-C (11.5 J/cm^2) treatments. Gamma irradiation (up to 20 kGy) did not induce formation of significant amounts of furan from any of the fatty acids studied. Storage of unsaturated fatty acid emulsions at 25 °C for 3 days led to the formation of furan (7–11 ng/mL) even without prior thermal or non-thermal treatments. pH significantly impacted furan formation with >3.5 times more furan formed at pH 9 than at pHs 3 or 6 during 3 days at 25 °C. The addition of Trolox, BHA, and propyl gallate had no significant effect on furan formation from linolenic acid while α-tocopherol and $FeSO_4$ promoted furan formation.
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1. Introduction

Furan (C_4H_4O) is classified by the International Agency for Research on Cancer as possibly carcinogenic to humans (IARC, 1995), and by U.S. Department of Health and Human Services (NTP, 2011) as "reasonably anticipated to be a human carcinogen." An FDA survey found that relatively high levels of furan were present in some thermally processed foods such as infant foods, soups, and meat products that underwent a retort process (FDA, 2009; Morehouse, Nyman, McNeal, Dinovi, & Perfetti, 2008). The levels of furan in those foods can be as high as 100–200 ng/g. Other surveys also indicated the presence of furan in cooked or thermally processed foods (Becalski & Seaman, 2005; Becalski et al., 2005). It is known that furan is produced from degradation and rearrangement of carbohydrates, polyunsaturated fatty acids, and ascorbic acid upon high temperature treatment (Locas & Yaylayan, 2004; Yaylayan, 2006).

The formation of furan due to thermal processing has been well studied (Becalski & Seaman, 2005; Crews & Castle, 2007; Fan, 2005a, 2005b; Hasnip, Crews, & Castle, 2006; Mariotti et al., 2012; Owczarek-Fendor et al., 2012). Many factors influence furan formation as a result of thermal treatments such as temperature, pH, and presence of phosphate and amino acids (Fan, Huang, & Sokorai, 2008; Van Lancker, Adams, Owczarek-Fendor, De Meulenaer, & De Kimpe, 2011). Phosphate generally promotes furan formation from simple sugars and ascorbic acid (Fan et al., 2008). Limacher, Kerler, Davidek, Schmalzried, and Blank (2008) showed that low (<1 μmol/mol) amounts of furan were formed from citric acid-phosphate buffered solutions of glucose, fructose, arabinose, and erythrose at pH 4, while at pH 7, significantly more furan was generated ranging from 2 to 17 μmol/mol. Our previous study (Fan, 2005a) found that low pH favored formation of thermally-induced furan from sucrose and ascorbic acid solutions. But for glucose solutions, less furan was formed at pH 3 than at pH 7. Some amino acids, especially alanine and serine, enhanced furan production by providing an additional formation pathway (Limacher et al., 2008; Van Lancker et al., 2011). Previous studies dealing with furan formation during thermal processing have involved use of high temperature such as pressure cooking, roasting, or otherwise, temperatures higher than 100 °C. There has been no report of furan formation at lower temperatures.

Fat (lipid) is one of the major components of most foods we consume every day, providing energy for the body and help to absorb lipid soluble vitamins in addition to other functions (Chow, 2007). Both animal- and plant-derived foods contain fat. The major compositions in fat are fatty acids even though fatty acids often exist as triglycerides or phospholipids. Traditionally,

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http://dx.doi.org/10.1016/j.foodchem.2014.12.002
0308-8146/Published by Elsevier Ltd.

foods are processed by the application of heat (i.e. thermal treatments, such as retorting *or* canning). However, in recent years, non-thermal processing technologies such as ionizing radiation and UV have been established (Zhang et al., 2011). The formation of furan from fatty acids due to heat treatment has been investigated. However, it is unclear whether furan can be formed from fatty acids upon non-thermal processing. It has been demonstrated that furan was produced from carbohydrates and ascorbic acid upon ionizing radiation (Fan, 2005a, 2005b). Whether ionizing radiation induces furan from fatty acids has not been investigated until now. UV-C irradiation also promoted formation of furan from carbohydrates and fruit juices (Fan & Geveke, 2007). Fructose is the main sugar that contributes to furan formation during UV-treatment (Bule et al., 2010; Fan & Geveke, 2007). Formation of furan from fatty acids due to UV has not been previously reported.

The objective of this present study was to investigate the formation of furan from fatty acids due to treatment with UV-C or gamma irradiation and storage, and the effects of antioxidants on furan formation during storage.

2. Materials and methods

2.1. Source of chemicals

Palmitic (99% purity), myristic (⩾99%), stearic acid (95%), oleic acid (99%), linoleic acid (⩾99), linolenic acid (⩾99), n-propyl gallate (⩾98), BHA (98% butyl hydroxyanisole), α-tocopherol (⩾95.5%), Trolox (97% (±)6-hydroxy-2,5,7,8 tetramethylchromane-2-carboxylic acid), ferrous sulfate (99%), absolute ethanol (99.8%), Tween 60, furan (99%) and furan-d4 (99%) were purchased from Sigma–Aldrich Co. (St. Louis, MO, USA).

2.2. Preparation of fatty acid emulsion

To prepare 0.1%, 0.2% and 0.4% fatty acid emulsions, different amounts (0.01, 0.02, and 0.04 g) of fatty acids and Tween 60 (0.02 g) were dissolved in 2 mL absolute ethanol first. Then 8 mL deionized water was slowly added into the ethanol while vortexing. The emulsions were then sonicated for 30 min using a sonicator (Model 2200, Branson Ultrasonics Corp., Danbury, CT). Volumetric droplet size of the emulsions was measured using a particle size analyzer (Model LA 950, Horiba Instruments Inc., Irvine, CA). A refractive index ratio of 1.48 was used to calculate the mean oil droplet size. The particle size distribution curve was unimodal with an average droplet size of 0.14 μm, D_{90} of 0.20 μm, and D_{10} of 0.09 μm while 100% of the particles was less than 0.34 μm. These oil-in-water emulsions were physically stable at ambient temperature for at least 3 days as the emulsions remained a similar droplet size (0.15 μm). Fatty acid emulsions were then treated with gamma irradiation, UV-C and heat (see below). The treatments did not alter droplet sizes of the emulsions. UV-C and irradiation doses were chosen to achieve 12-log reduction of bacterial pathogens based on our previous studies (Fan & Geveke, 2007).

2.3. Thermal treatment

Different fatty acid emulsions (0.2%, 1 mL) were placed in 4 mL vials and sealed using 3 mm thick Tuf-Bond Teflon septa (Thermo Scientific, Bellefonte, PA) and cap. The vials were submerged into a 120 °C silicone oil bath. The vials were positioned so that only the bottom half of the vials were submerged into the oil bath. After a 25 min treatment, the vials were cooled in ice water before d_4-furan standard (20 ppb) was added into the vial through the septum using a 10 μL syringe. Furan and d_4-furan in the vials were then measured.

2.4. Gamma irradiation

Irradiation of fatty acid samples in sealed glass vials was conducted using a self-contained, Lockheed Corporation ^{137}Cs gamma radiation source with a dose rate of approximately 0.074 kGy min^{-1}. Samples were irradiated to doses of 6 kGy gamma rays. During irradiation, the temperature of the treatment chamber where samples were placed was maintained at 10 ± 2 °C by injecting the gas phase from a liquid nitrogen tank. Alanine dosimeters (Far West Technology Inc., Goleta, CA, USA) were placed along with samples to verify the doses. The free radical signal induced in response to radiation was quantified by inserting the alanine dosimeters into an Escan EPS analyzer (Bruker Instruments Inc., Billerica, MA, USA), and compared with a standard curve. Measured dose was 5.74 kGy.

2.5. UV-C treatment

UV-C treatment of fatty acid emulsion was performed at ambient temperature (~22 °C). UV-C was generated from a 16 inch long Philips model TUV PL-L 35W germicidal fluorescent lamp mounted in a customized fixture (CureUV.com, Delray Beach, FL). A Thermix stirrer, Model 120mR stir plate (Fisher Scientific, Nepean, Ontario, Canada) was placed next to the UV-C apparatus. Emulsions (1 mL) of each fatty acid were placed into a 3-mL quartz cuvette (Spectrocell, Oreland, PA, USA) containing a mini magnetic stir bar, and the cuvette was sealed using a septum and cap. The cuvettes allowed 90% of UV-C to transmit through the quartz wall. During the 25 min UV treatment, the cuvettes containing the samples were set straight up on the stir plate on a marked line perpendicular to the UV-C box (Fan & Geveke, 2007). The samples were stirred at a speed setting of 2 during UV treatment. UV-C intensity was 8.5 mW/cm^2 as measured at the same distance as the cuvettes using a UVX-25 radiometer (UVP Inc., Upland, CA, USA). The UV incident dose was calculated with the following equation: UV dose (J/cm^2) = irradiance (mW/cm^2) × exposure time (s)/1000. During the treatment, sample temperature did not exceed 30 °C.

2.6. Effect of storage, concentration of linolenic acid, and pH on furan formation

Samples of fatty acid emulsion (1 mL, 0.2%) in the sealed vials were stored in a 25 °C incubator for up to 6 days. Furan was analyzed at 0, 1, 3, and 6 days of storage. To study the effect of linolenic acid concentration, 0.1%, 0.2% and 0.4% linolenic acid emulsions were prepared, and stored at 25 °C for 3 days. To evaluate the effect of pH on furan formation, linolenic acid (0.2%) emulsion was prepared as described previously except 100 mM phosphate buffers at 3 pH values (3, 6, and 9) were used. Samples (1 mL) were stored at 25 °C for 3 days before furan was analyzed.

2.7. Effect of antioxidants and ferrous sulfate on linolenic acid during storage

Ten mM BHA, Trolox, proposal gallate, α-tocopherol, and ferrous sulfate solutions were prepared in 20% ethanol. The solutions were then diluted 10 times with 0.22% linolenic acid emulsion in 20% ethanol to obtain a final concentration of ~1 mM antioxidants/ferrous sulfate in 0.2% linolenic acid emulsion. Linolenic acid (0.2%) emulsion with 20% ethanol was used as a control (no antioxidant). The samples (1 mL each) were placed into 4 mL vials and stored in an incubator set at 25 °C for 3 days.

2.8. Analysis of furan

Preparation of stocking and working solutions has been described earlier (Fan, 2005a). After UV-C, gamma irradiation,

thermal or storage treatments, all samples were spiked with 20 ng/mL d_4-furan. Furan and d_4-furan were analyzed as described earlier (Fan, 2005a) with minor modification. Samples in the 3-mL cuvettes (for UV-C samples) or 4 mL glass vials were incubated at 35 °C for 25 min on a Corning heat/stir plate (Supelco, Bellefonte, PA, USA) before a fiber (85 μm Carboxen-PDMS) was inserted into the headspace of a vial. After 20 min of extraction time, the SPME fiber was inserted into the GC injection port at 250 °C and held for 5 min to desorb volatile compounds. An Agilent 6890N/5973 inert GC-MSD (Agilent Technologies, Palo Alto, CA, USA) equipped with a 30 m, 0.32 mm i.d., 20 μm coating HP-PLOT Q column (Agilent Technologies, Palo Alto, CA, USA) was used to detect and analyze furan. The temperature of the GC oven was set at 60 °C for 2 min, increased to 250 °C at 20 °C/min, and held for 4 min at the final temperature. Helium as the carrier gas was set at a flow rate of 39 cm/s. The transfer line was held at 250 °C during the entire run. Furan and d_4-furan were identified by comparison of spectra of the sample compounds with those of standards. The m/z 39 and 68 ions and the ratio of 39/68 were used for the confirmation of furan while m/z 41 and 72 ions and the ratio of 41/72 were used for the confirmation of d_4-furan. Ions 68 and 72 were used as the quantifiers for furan and d_4-furan, respectively. Furan was quantified using standard curves established for fatty acid emulsions containing 20% of ethanol and 0.2% Tween 60 in the 3 mL cuvette and 4 mL glass vials.

2.9. Statistical analysis

Treatments were repeated 4 times. Data were subjected to statistical analysis using SAS Version 8.2 (SAS Institute, Cary, NC, USA). The differences between treatments were analyzed by the Duncan's Multiple Range Test using the general linear model. Only significant differences ($p < 0.05$) are discussed unless stated otherwise.

3. Results and discussion

3.1. Optimization of extraction condition

A SPME procedure has been optimized in terms of SPME type, extraction time, desorption time, and extraction temperature (Fan, 2005a; Fan et al., 2008). We also tested the effect of NaCl addition on the extraction efficiency of the SPME. Up to 0.5 g/mL NaCl had no effect on the extraction efficiency of furan (data not shown). Three types of septa for sealing the glass vials were also tested including 1.5 mm thick PEFE/Silicone from Supelco (Bellefonte, PA), 1.5 mm thick Septum PTFE/Silicone from Kimble-Kontes (Vineland, NJ) and Tuf-Bond Teflon (2.5 mm in thickness) (Bellefonte, PA). The thicker septum (Tuf Bond) was best in preventing leakage of furan after puncturing with the SPME needle during extraction. Therefore, Tuf-Bond septa were used in the present study. Our preliminary results showed that the presence of ethanol significantly reduced the SPME extraction efficiency of furan as compared with the standard curve established in water. Therefore, standard curves were established in fatty acid emulsions containing 20% ethanol. The types of fatty acids had little effect on the extraction efficiency.

3.2. Formation of furan due to thermal processing

There was little furan formed from myristic, palmitic, stearic or oleic acid after 25 min thermal treatment at 120 °C (Fig. 1). Samples not treated with 120 °C did not produce furan. Significant amounts of furan (149.9 and 239.7 ng/mL) were only formed from linoleic acid and linolenic acid after treatment. The highest amount of furan was found in linolenic acid. Even though oleic acid is also an unsaturated fatty acid, little furan was formed upon thermal treatment. Becalski and Seaman (2005) demonstrated that linolenic acid produced 5 times more furan than linoleic acid when heated at 118 °C for 30 min. Our results confirmed earlier reports of furan formation from polyunsaturated fatty acids upon thermal treatments (Becalski & Seaman, 2005; Locas & Yaylayan, 2004).

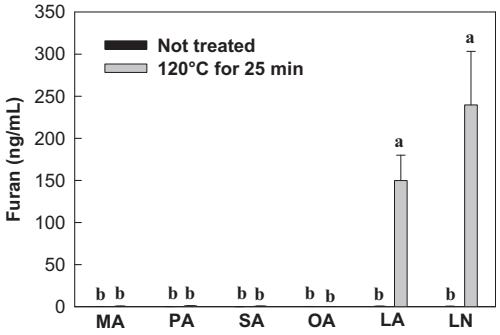


Fig. 1. Formation of furan from emulsion of fatty acids treated with 120 °C for 25 min. MA = myristic acid, PA = palmitic acid, SA = stearic acid, OA = oleic acid, LA = linoleic acid, LN = linolenic acid. Standard bars represents standard deviations ($n = 4$). Bars with same letters are not significant different ($p > 0.05$).

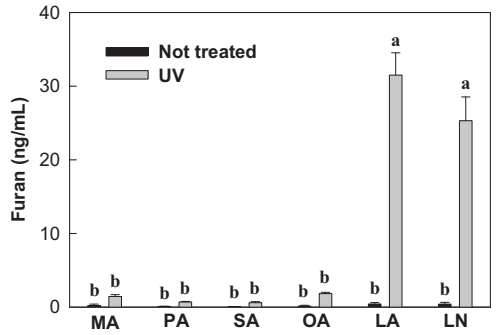


Fig. 2. Effect of UV-C treatment (11.5 J/cm^2) on furan formation from emulsion of fatty acids. MA = myristic acid, PA = palmitic acid, SA = stearic acid, OA = oleic acid, LA = linoleic acid, LN = linolenic acid. Standard bars represents standard deviations ($n = 4$). Bars with same letters are not significant different ($p > 0.05$).

3.3. Formation of furan due to UV-C treatment

The UV-C dose that the samples received was estimated to be 11.5 J/cm^2. UV-C induced furan formation mainly from linoleic and linolenic acids (Fig. 2). There was no significant difference in the levels of furan between linoleic and linolenic acid, with 25.3–31.5 ng/mL furan in the two fatty acid emulsions after UV-C treatments. For the first time, we have shown that UV-C could induce furan formation from polyunsaturated fatty acids, as was the case with thermally induced furan (Becalski et al., 2005; Märk, Pollien, Lindinger, Blank, & Märk, 2006). However, compared with the thermal processing (120 °C for 10 min), significant lower amounts of furan were produced after UV-C treatment at 11.5 J/cm^2. Also, the amounts of furan formed were several times less than those formed from 5% fructose after the same dose of UV-C exposure (data not shown).

3.4. Formation of furan during post-irradiation storage

Little furan was found in any of the fatty acids emulsion immediately after 6 kGy of gamma irradiation (data not shown).

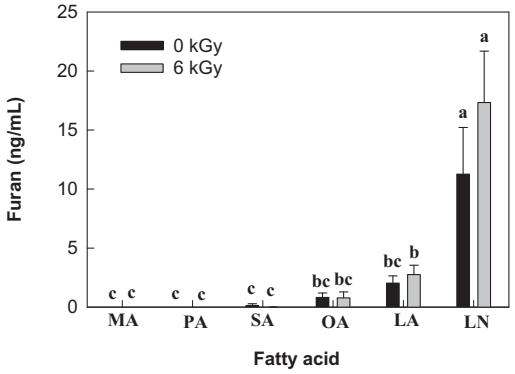


Fig. 3. Formation of furan from different type of fatty acids treated with or without 6 kGy radiation. The samples were analyzed after 3 days of storage at 25 °C. MA = myristic acid, PA = palmitic acid, SA = stearic acid, OA = oleic acid, LA = linoleic acid, LN = linolenic acid. Vertical bars represent standard deviations (n = 5). Bars with same letters are not significant different (p > 0.05).

Increases in irradiation doses up to 20 kGy did not yield significant amounts of furan either as measured on the day of irradiation (data not shown), suggesting that irradiation did not induce formation of furan from fatty acids.

The samples of fatty acid emulsion were then stored at 25 °C for 3 days after irradiation (6 kGy) to study whether irradiation promoted furan formation during post-irradiation storage. After 3 days at 25 °C, there were little furan formed from myristic, palmitic or stearic acids regardless of irradiation (Fig. 3). However, in both irradiated and non-irradiated samples, low levels of furan were formed from oleic acid, and higher amounts of furan were formed from linoleic and linolenic acid emulsions. Compared to amount of furan formation from linoleic acid, 5.6 times more furan was formed from linolenic acid regardless of irradiation treatments. It appears that the formation of furan from unsaturated fatty acids increased with increasing degree of unsaturation. During the post-irradiation storage period, irradiated linoleic and linolenic acid did not produce significantly (p > 0.05) more furan than the non-irradiated samples.

3.5. Factors affecting furan formation during storage at 25°C

Storage of fatty acid emulsion at 25 °C had a significant effect on furan formation (Fig. 4A). The longer the storage time, the more furan formed. Our results showed for the first time that furan can be produced without the involvement of high temperature treatment. The samples were stored at 25 °C and did not exceed 35 °C even during the SPME extraction time. Previous studies dealing with thermally-induced furan formation employed temperature of 100 °C or higher (Becalski & Seaman, 2005; Crews, Hasnip, Roberts, & Castle, 2007; Hasnip et al., 2006; Locas & Yaylayan, 2004; Mariotti et al., 2012).

The concentration of linoleic acid also affected furan formation during storage at 25 °C. The higher the concentration, the greater the amount of furan formed (Fig. 4B). pH had a significant effect on furan formation from linolenic acid during storage at 25 °C (Fig. 4C). The higher the pH, the more furan formation, particularly at pH 9. There was about 5.5 times more furan formed at pH 9 than at pH 3. These results seem to agree with our results on thermally-induced furan, i.e. more furan was produced in linoleic acid emulsion at pH 6 than at pH 3 upon thermal treatment (Fan et al., 2008). However, a study by Crews et al. (2007) demonstrated that furan formation from green beans and a bean-based vegetable mixture decreased with increasing pH when the samples were heated at 120 °C for 60 min. Perhaps, the effect of pH on furan formation depends on the type of precursors and treatment conditions.

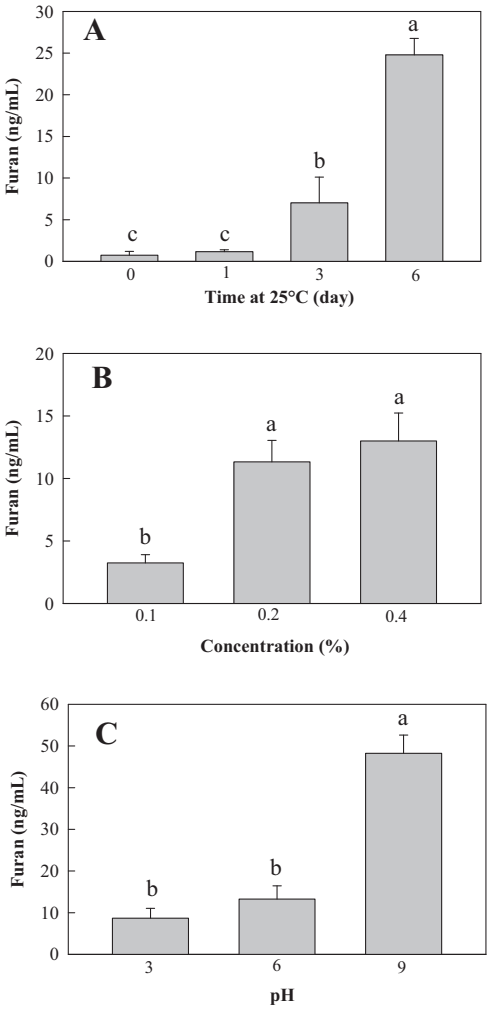


Fig. 4. Effect of storage at 25 °C (A), concentration (B) and pH (C) on formation of furan from an emulsion of linolenic acid. For the storage and pH effects, 0.2% linolenic acid was used. For the pH and concentration effect, furan was analyzed after 3 days of storage. Standard bars represents standard deviations (n = 4). Bars with same letters are not significant different (p > 0.05).

3.6. Effect of antioxidants and ferrous sulfate on furan formation from linolenic acid during storage at 25°C

It has been hypothesized that thermally induced furan from lipids is a result of oxidative degradation of fatty acids via 4-hydroxy-2-butenal as an intermediate compound (Märk et al., 2006; Yaylayan, 2006). If furan is formed from lipid oxidation, one can expect that antioxidants that are capable of scavenging free radicals should reduce the formation of furan. Furan (~10 ng/mL) was formed from 0.2% linolenic acid during 3 days of storage at 25 °C. Antioxidants such as BHA, Trolox and propyl gallate had no significant effect on furan formation from linolenic acid (Fig. 5). The reason for the ineffectiveness of the antioxidants in reducing furan formation from linolenic acid is unclear. Perhaps the pathway of furan formation from polyunsaturated fatty acids is not a simple oxidation process. Different mechanisms may exist, and these need further studies.

Ferrous sulfate greatly increased furan formation. At least 4 times more furan was formed from samples containing ferrous ions compared to the control. It is known that ferric and ferrous ions promote lipid oxidation (Braughler, Duncan, & Chase, 1986). Autoxidation of ferrous converts ferrous to ferric (Bucher, Tien, & Aust, 1983). An earlier study (Owczarek-Fendor et al., 2010)

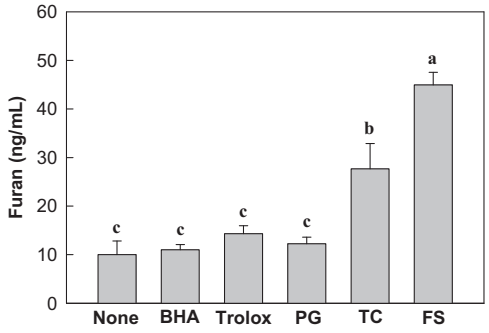


Fig. 5. Effect of antioxidants and ferrous sulfate on furan formation from an emulsion of linolenic acid (0.2%) during 3 days of storage at 25 °C. BHA = butyl hydroxyanisole, Trolox = (±)-6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid, PG = n-propyl gallate, TC = α-tocopherol, FS = ferrous sulfate. Standard bars represents standard deviations ($n = 4$). Bars with same letters are not significant different ($p > 0.05$).

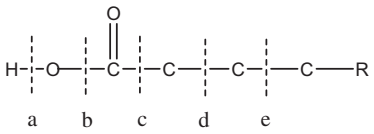
showed that ferric or ferrous ions did not have a catalytic effect on furan formation from ascorbic acid at pH 4. Becalski and Seaman (2005) also found that the addition of ferric ion did not affect the formation of furan from ascorbic acid in unbuffered aqueous solution, but promoted furan formation in sodium ascorbate solution. Märk et al. (2006) found that the presence of ferric ions reduced the levels of furan from linolenic acid by 47% while promoted furan formation from linoleic acid by 79%. It seems that there is contradiction on the effect of ferric ions on furan formation. It is unclear whether the difference is caused by the ion difference (ferric vs. ferrous) or other factors.

Furan was not formed directly from α-tocopherol alone (data not shown). However, the presence of α-tocopherol significantly increased furan formation from linolenic acid. It has been reported that α-tocopherol has antioxidant activity at low concentrations but prooxidant activities at high concentrations (Cillard, Cillard, Cormier, & Girre, 1980; Koskas, Cillard, & Cillard, 1984). Huang, Frankel, and German (1994) showed that α-tocopherol had a pro-oxidant effect in oil-in-water emulsions. Perhaps the promotive effect of α-tocopherol on furan formation is due to its pro-oxidant effect. More studies should be conducted to evaluate the effect of α-tocopherol concentration. Märk et al. (2006) found that α-tocopherol (1.2%) reduced thermally-induced furan formation from linolenic acid by 20%. Our present study for the first time demonstrated that addition of vitamin E to fatty acids could lead to more furan formation.

Trolox is a water soluble analog of α-tocopherol. Because of the hydrophilic properties of Trolox, the antioxidant efficiency of α-tocopherol and Trolox are different: Studies have found that Trolox was more effective than α-tocopherol in inhibiting oxidation of linoleic acid emulsion (Frankel, Huang, Kanner, & German, 1994; Huang, Hopia, Schwarz, Frankel, & German, 1996). Our results showed that Trolox and α-tocopherol behaved differently as α-tocopherol increased the formation of furan while Trolox did not. The difference may be due to the diffusion of Trolox into water phase and into mixed micelles. BHA and propyl gallate, hydrophilic antioxidants, may behave similarly as Trolox.

Addition of BHA, Trolox and propyl gallate did not have significant effect on furan formation. It is unclear why the compounds had no effect even though they are common antioxidants. All three compounds are hydrophilic antioxidants and as such they may dissolve in the water phase. To be effective in inhibiting lipid oxidation, they have to accumulate in the interface between the two phases in the emulsion droplets (Frankel et al., 1994). It is also possible that some of the antioxidant effects were related to the presence of ethanol in the emulsions or even to the amount of oxygen dissolved in the emulsion during vortexing.

Our previous study (Fan, 2005a) showed that gamma irradiation induced formation of large amounts of furan from simple sugars and ascorbic acid. Our present study demonstrated that gamma irradiation did not induce formation of furan from fatty acids. It seems that the mechanisms for furan formation due to irradiation vary depending on the type of precursors. When fatty acids are irradiated, the possible sites of cleavage occur near the carbonyl bond at sites as indicated below (Delincee, 1983; Fan, 2012; Nawar, 1983).



As a result, the major radiolytic products of fatty acids are carbon dioxide, hydrogen, carbon monoxide, hydrocarbons (alkanes and alkenes) and long chain (C_n) aldehydes (Lee & Ahn, 2003; Nawar, 1986). 2-Alkyl- and 2-alkenylcyclobutanones, unique radiolytic products, are produced from fatty acids and triglycerides due to clearage of the acyl-oxy bound (Nawar, 1986; Verniest et al., 2004).

Although the exact mechanisms for furan formation are unclear, it has been hypothesized that at least some furan is produced by the combination of two C_2 fragments (e.g. acetaldehyde and glycolaldehyde) (Limacher et al., 2008; Van Lancker et al., 2011). Irradiation of fatty acids produced little (if any) C_2 aldehydes especially in the absence of oxygen (Delincee, 1983; Nawar, 1983). Therefore, it is understandable that irradiation did not induce furan formation from fatty acids.

For the first time, our results showed that UV-C induced furan formation from polyunsaturated fatty acids. It has been proposed that thermally-induced furan originates through lipid oxidation process from 2-butenal, a direct oxidation product of unsaturated fatty acids, with further oxidation to 4-hydroxy-2-butenal, cyclization of 4-hydroxy-2-(*Z*)-butenal, and subsequent dehydration (Yaylayan, 2006). Addition of 2-butenal into sunflower oil led to elevated formation of furan upon heating (120 °C, 20 min) (Owczarek-Fendor et al., 2010). Luna, Morales, and Aparicio (2006) showed that acetaldehyde and 2-butenal among others were the major volatile compounds during the UV-B irradiation of olive oil. Our results suggested that UV-C dramatically accelerates the oxidation process of fatty acids leading to formation of furan.

Our data, for the first time, showed that furan can be formed from polyunsaturated fatty acids without the involvement of high temperature. The results may have some potential implications in food. For example, consumption of dietary supplements of polyunsaturated fatty acids has increased over the last few decades due to the realization of their health benefits (Blasbalg, Hibbeln, Ramsden, Majchrzak, & Rawlings, 2011; Eisenberg et al., 1998; Serini, Fasano, Piccioni, Cittadini, & Calviello, 2011) although there is some evidence of possible toxicity of polyunsaturated fatty acids and their oxidative products (Arab-Tehrany et al., 2012; Patterson, Wall, Fitzgerald, Ross, & Stanton, 2012). Future studies may be conducted to evaluate whether long term storage of the fatty acids in ambient temperature will lead to formation of furan or if the formation of furan will have potential health effects. Furthermore, possible formation of furan from fat-containing foods such as oils, nuts and milk powder that are often stored in ambient temperatures may be investigated during a long-term storage.

The experiments in the present study were conducted using emulsion of free fatty acids. Future work may be conducted to investigate whether lipids such as triacylglycerols and fatty acid

methyl esters behave similarly as free fatty acids in response to UV, irradiation and storage. Furthermore, the possible formation of furan in real foods such as linseed oil that contain high amounts of unsaturated fatty acids may be conducted during storage at abused (elevated) temperatures. Study by Owczarek-Fendor et al. (2010) suggested that oils containing linolenic acid were able to generate significant amounts of furan upon heating if the oils were oxidized.

4. Conclusions

Our results demonstrated that furan was produced from polyunsaturated fatty acids during thermal and UV-C treatment. Ionizing irradiation did not directly induce furan formation from any of the fatty acids. Furan was also produced from linolenic acid emulsion during storage at 25 °C, and the longer the storage, the more furan was formed. pH had a significant effect on furan formation from linolenic acid with more furan produced at pH 9 than at pHs 3 or 6. The antioxidants tested did not show any inhibitory effect on furan formation. In fact, α-tocopherol increased furan formation. The exact mechanism(s) for furan formation from fatty acids as affected by antioxidants need further study.

Acknowledgments

I am grateful to Drs. Gerald Sapers and Steve Lehotay for critical reading of the manuscript, and Kimberly Sokorai, Audrey Thomas-Gahring and Stefanie Simon for technical assistance.

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